Sputter Deposition of Metallic Sponges

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January 18, 2002

U.S. Department of Energy

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Abstract

Metallic films are grown with a sponge-like morphology in the as-deposited condition using planar magnetron sputtering. The morphology of the deposit is characterized by metallic continuity in three dimensions with continuous porosity on the sub-micron scale. The stabilization of the metallic sponge is directly correlated with a limited range for the sputter deposition parameters of working gas pressure and substrate temperature. This sponge-like morphology augments the features as generally understood in the classic zone models of growth for physical vapor deposits. Nickel coatings are deposited with working gas pressures up to 4 Pa and for substrate temperatures up to 1100 K. The morphology of the deposits is examined in plan and in cross-section with scanning electron microscopy. The parametric range of gas pressure and substrate temperature (relative to absolute melt point) for the deposition processing under which the metallic sponges are produced appear universal for many metals, as for example, including gold, silver, and aluminum.

Introduction

The growth of thin-film metallic sponges is of interest in several electrochemical applications, for example, conductive porous electrodes for gas transport and processing.[1-2] Determination of the experimental parameters needed to yield metallic sponges should be tractable for physical vapor deposition processes. The general observations as how to stabilize the basic coating morphologies are found in the classic zone model and experiments of film growth.[3-9] It is known that morphologies in structure can range from porous columnar to dense polycrystalline as the process conditions are varied for either sputter deposition or evaporation. For example, the transition through four zones of film growth with increased substrate temperature (and working gas pressure) is found and described by Thornton for metal coatings sputter deposited using cylindrical magnetrons.[4-5] Zone 1 is characterized by a structure consisting of tapered crystallites separated by voids. A transition Zone T is characterized by a structure consisting of densely packed fibrous grains and a smooth surface. Zone 2 next features columns that are continuous from the substrate to a surface characterized by crystalline facets. Finally, Zone 3 represents the recrystallized grain structure. The primary effect of increased temperature is an enhancement of adatom surface diffusion and minimal adsorbed working gas. There is some indication that porous structures can result at high temperatures from shadowing if the deposition conditions favor the formation of large aggregates or from favorable growth directions that can yield isolated crystallites.[5, 9-10] However, there is no general reference to the three-dimensional structure of a sponge. That is, a polycrystal with continuous open porosity but without the definitive columnar features characteristic of vapor deposits. Herein, conditions for deposition are resolved that produce the sponge morphology augmenting the zone models of structure for

the growth of thin films and thick coatings. For sputter deposition using planar magnetrons, the general conditions are an increased working gas pressure and an intermediate substrate temperature approximately half the absolute melting point. Examples of the sponge morphology in as-deposited coatings are cited, as seen in Figure 1 for gold as well as for silver. [1] Details for the stabilization of the metallic sponge are described within the context of the zone model of structure for growth of coatings and are presented for planar magnetron deposits of nickel that are up to 10 μm in thickness.

Experimentals

The effects of working gas pressure and substrate temperature are the key parameters in the assessment of growth modes for sputter deposited coatings. The deposition of the metallic coatings is conducted using 6.4 cm diameter planar magnetrons operated in the dc mode. The configuration of the iron-neodymium-boron magnets within the planar magnetron is unbalanced. The vacuum chamber is cryogenically pumped to a base pressure of 2 μPa (1.5_10^{-8} Torr). A 25-40 cc min^{-1} flow (q_{gas}) of the working gas is then initiated prior to substrate heating. The working gas is the boil off from a dewar of liquid Argon. The gas pressure (p_{gas}) range is in multiples of 0.67 Pa (5 mTorr) to 4 Pa (30 mTorr). The substrates are silicon wafers with a 0.2-0.4 μm thick surface layer of silicon nitride. The substrates are mounted to the obverse side of a tantalum substrate platform. Thermocouples are attached to both the obverse and reverse sides of the substrate platform. The temperature variance across the substrate is less than 5 K (°C). Once the selected conditions of gas pressure and flow are obtained, the substrate platform is heated from

the reverse side using a resistive heater. A Variac^{TM} supply is used to power the Boralectric^{TM} (boron-nitride) resistive heater. The substrate temperature (T_{sub}) is experimentally found to be logarithmically proportional to the applied heater power (P_{heat}), that is, $T_{sub} \_ \log(P_{heat})$. The substrate platform is insulated with a Macor^{TM} spacer and is contained within a water-cooled copper shroud. This configuration facilitates substrate heating to elevated temperatures within the copper shroud while maintaining a temperature below 50°C outside of the shroud. The planar magnetrons are situated 11 cm beneath the substrate surface. Typically, deposition rates up to 40 nm_min^{-1} are produced from applied forward powers of 8 W_cm^{-2} for coatings of nickel that are sputtered from a 0.9999 pure target.

The 3-10 µm coatings are examined in plan view and selectively in cross-section (after fracture) using a scanning electron microscope. The images are formed from a combination of backscattered electrons and secondary electrons. A lower accelerating voltage of 5 kV for the beam facilitates the topological imaging of the surface features.

Experimental Results and Analysis

In general, the results obtained for nickel with a melt temperature (T_{melt}) of 1455°C are consistent with the zone model for growth of sputter deposited coatings. For example, a nickel coating deposited at 10 mTorr - 220°C is characteristic of the upper bound to Zone 1, where an increase in packing density is seen for the tapered crystallites. Results for nickel samples deposited over a working gas pressure range of 5 to 25 mTorr and substrate temperatures of 400 to 900°C are shown in the plan view images of Fig. 2. As the substrate temperature is increased above 300°C,

a transition in structure to Zone T is seen, e.g., at 20 mTorr - 445°C. Faceting of the surface for a fully columnar structure becomes prevalent above 500°C with the higher gas pressures, e.g., as seen at 25 mTorr - 600°C, indicating a transition to Zone 2. A recrystallized structure appears at the highest temperatures, e.g., 5 mTorr - 800°C, for Zone 3. A new morphology, i.e., the metallic sponge, is seen in Fig. 2 corresponding to deposition conditions (e.g., at 10 mTorr - 650°C) that are between the Zone T and Zone 2 structures.

The stabilization of the sponge morphology can be viewed as a transition between Zone T and Zone 2. The transition in structure between the characteristic zones of growth with the increase of substrate temperature in approximate 200°C increments is seen in the cross-section images of nickel coatings deposited at (Fig. 3a) 10 mTorr - 220°C, (Fig. 3b) 20 mTorr - 445°C, (Fig. 3c) 10 mTorr - 660°C, and (Fig. 3d) 10 mTorr - 810°C. These cross-section images (Figs. 3a-d) reveal the morphological evolution from Zone 1 then Zone T through the metallic sponge to Zone 3. The temperature range to stabilize the metallic sponge for nickel appears most broad at 10 mTorr. The intermediate, working gas pressure of 10 mTorr appears to influence scattering effects that enhance growth along crystalline directions other than perpendicular to the plane of the substrate. The metallic sponge accentuates the onset of porosity as found for high temperature deposits as previously reviewed [5, 9-10] in the Introduction. The zone for growth of the metallic sponge then narrows with either an increase or decrease from the intermediate gas pressure of 10 mTorr. If the substrate temperature is normalized to the absolute temperature of the melting point, then the zone for growth of the metallic sponge in nickel can be referenced for other metals. For comparison, the nickel results with a nominal range of 0.48-0.57 for the $T_{sub\_}T_{melt}^{-1}$ ratio are confirmed in Fig. 1 where the metallic sponge structure is stabilized for gold

coatings deposited at 5 mTorr - 300°C (i.e., a $T_{sub}\_T_{melt}^{-1}$ of 0.43) as well as silver coatings

deposited at 15 mTorr - 400°C (i.e., a $T_{sub}\_T_{melt}^{-1}$ of 0.54).

Discussion

The formation of the metallic sponge morphology can be achieved through other deposition

process methods. For example, millimeter-sized pores can be formed through an electron-beam

directed vapor deposition process. Metals are evaporated onto an open-cell polymer foam

template and then post-deposition processed to remove the polymer.[11] Similarly, methods are

available that reduce metal-polymer blends to yield micron-size pores in thick films. For

example, Osmonics[TM] produces silver sheet with continuous pores less than 5 μm in size. The

use of intermittent steps to the deposition process is a demonstrated method of producing a high

density of micron-sized holes in nickel and silver films through photolithographic patterning and

etching.[12-13] However, the sputter deposition process described for the present results yields a

coating that has a continuous, sub-micron porosity in the as-deposited structure.

The temperature range over which the metallic sponge is formed corresponds to one-half

the melting point of the metal. At this temperature, although recrystallization and grain growth

occur in the coating, surface diffusion still dominates. The result is the onset of faceting that is so

prevalent for the structure of Zone 2. It's postulated that enhanced surface diffusion with some

recrystallization leads to the growth of grains that are not perpendicular to the substrate plane.

That is, faceted planes will grow obliquely to the substrate surface and at a rate competitive with

the textured normal growth seen at lower deposition rates. The use of a raised working gas

pressure further adds to scattering of the sputtered species and an increased flux of non-normal incident arrival. Together, the use of an intermediate gas pressure and an elevated substrate temperature yield the metallic sponge morphology. The possibility for stabilizing a metallic sponge structure is suggested by Thornton, wherein a superimposed structure can result from structures normally associated with individual zones, in this case Zones T and 2. [6-8] Since it is known that working gas pressure affects the extent of the Zone T by reducing the energy of sputtered species and reflected ions while scattering the arrival of sputtered species to more oblique angles [8], the superposition of Zone T (with Zone 2) in forming the metallic sponge zone further supports the present result that working gas pressure determines the extent of this new zone. The location of the metallic sponge zone is consistent with the transition temperature of one-half the melting point between Zones T and 2 in the revised structure zone model that assesses conditions of energetic particle bombardment (in lieu of gas pressure). [14-15] For PVD processes, high deposition rates are generally considered as greater than 10 nm_s^{-1} whereas low deposition rates are less 1 nm_s^{-1}. In this study, the deposition rate can't be considered as high and is an unlikely contributing cause for the sponge morphology. [5]

Summary

The stabilization of the sponge (S) morphology can be viewed within the context of the zone model for metal coatings as a new transition Zone S between Zones T and 2. The structure is characterized by continuity in three dimensions with continuous porosity on the submicron scale. This structure is observed in results presented for metals as gold, silver and nickel across a range

in temperatures that correspond with 0.48-0.57 of the absolute temperature of melting for an intermediate range of working gas pressures.

Acknowledgments

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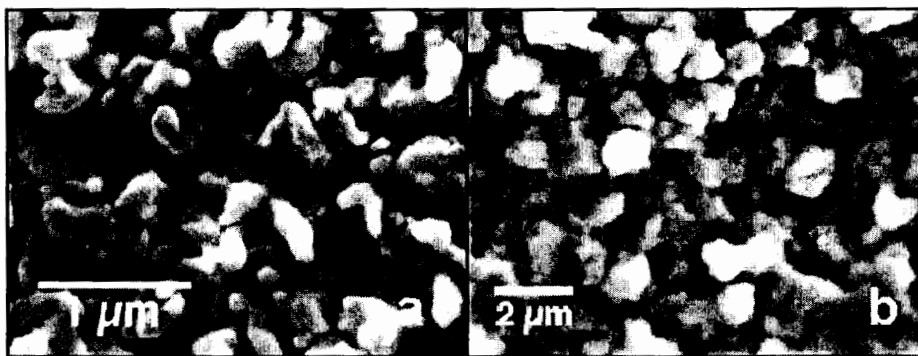
Figure 1. The sponge-like morphology of sputter deposited coatings of (a) gold and (b) silver are revealed in these plan view images.
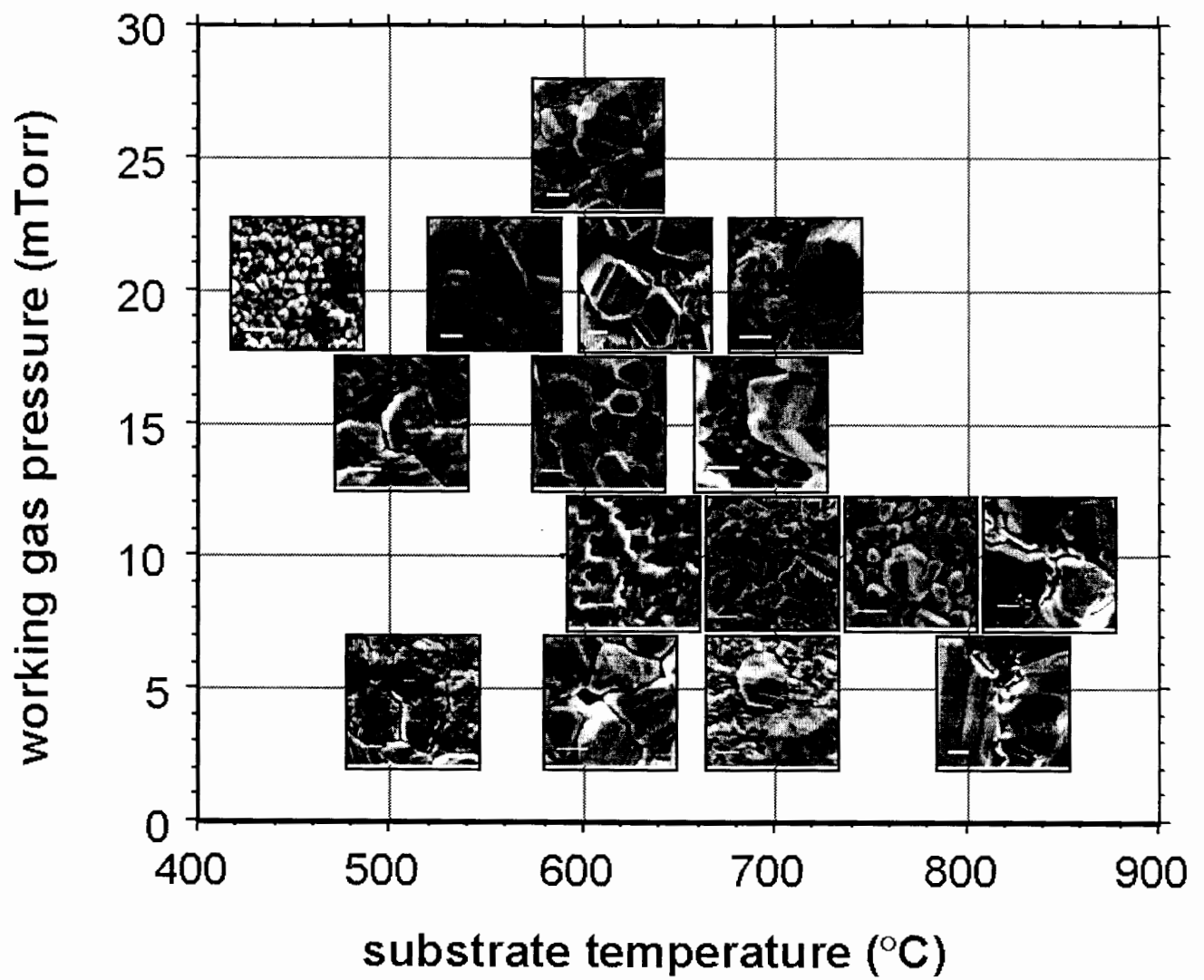
Figure 2. Plan view images of the nickel coatings deposited as function of working gas pressure (mTorr) and substrate temperature (˚C). Bar = 0.5 μm.
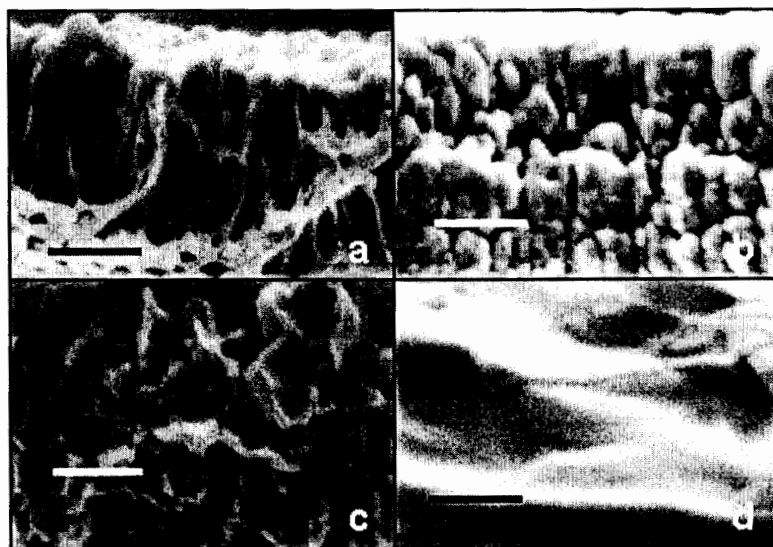
Figure 3. Cross-section images of the nickel coatings as sputter deposited at (a) 10 mTorr - 220°C, (b) 20 mTorr - 445°C, (c) 10 mTorr - 660°C, and (d) 10 mTorr - 810°C. Bar = 0.5 μm.